

REPORT DOCUMENTATION PAGE

(2)

AD-A252 485

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTION None		
2a. SECURITY CLASSIFICATION AUTHORITY SCT	3. DISTRIBUTION STATEMENT Unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE (SCHEDULE 192)			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 12	5. MONITORING ORGANIZATION REPORT NUMBER(S) Office of Naval Research		
6a. NAME OF PERFORMING ORGANIZATION Univ. of Nebraska-Lincoln	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 632 Hamilton Hall Univ. of Nebraska Lincoln, NE 68588-0304	7b. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 111 800 N. Quincy Street Arlington, VA 22217-5000	3PO	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1494	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. : WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Holographic Grating Relaxation & Photon Correlation Spectroscopic Studies of Viscoelastic Liquids Above the Glass Transition			
12. PERSONAL AUTHOR(S) C. H. Wang and S. S. Gong			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 92/6/1	15. PAGE COUNT 3
16. SUPPLEMENTARY NOTATION Polymer Preprint			
DEFENSE TECHNICAL INFORMATION CENTER 9215852			
17. COSATI CODES FIELD GROUP SUB-GROUP	18. SUBJECT TERMS (Continued)		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Photon correlation spectroscopic (PCS) and holographic grating relaxation (HGR) techniques are used to measure the dynamics of density fluctuations in liquid orthoterphenyl, salol and poly(propylene glycol) oligomers in both the normal and supercooled liquid regimes down to their glass transition temperatures. In the PCS study a strongly temperature dependent nonhydrodynamic mode due to structural relaxation is observed in each of the above mentioned glass forming liquid. The shape of the nonhydrodynamic mode is nonexponential and can be fit to a stretch exponential function for each liquid. The nonhydrodynamic mode measured in PCS is shown to be the dynamic longitudinal compliance of the liquid. The tracer diffusion coefficients of camphorquinone in the above glass forming liquids do not obey the Stokes-Einstein equation. The slowness of the structural relaxation of the host liquid and the finite size of the tracer are identified to be the cause for the departure from the Stokes Einstein equation.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Joanne Miller		22b. TELEPHONE (Include Area Code) (202) 696-4409	22c. OFFICE SYMBOL

92 6 16 180

**Holographic Grating Relaxation and Photon Correlation
Spectroscopic Studies of Viscoelastic Liquids
Above the Glass Transition
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Introduction

The viscoelastic properties of polymeric and low molecular weight glass-forming liquids are greatly influenced by the onset of the glass transition process. In addition the dynamics of density fluctuations is closely associated with the viscoelastic response of the liquid and thus it is strongly affected by the glass transition.

The dynamics of density fluctuations of the viscoelastic liquid above the glass transition temperature (T_g) can be probed by the techniques of dynamic light scattering. In particular, density fluctuations can be investigated by the photon correlation spectroscopic (PCS) technique in the dynamic range of 10^{-6} - 10^2 s.

The time correlation function of the density fluctuations $C(t)$, above T_g , is characterized by a highly nonexponential shape. This nonexponential shape is associated with the α -relaxation process in the glass-forming liquid. The α -process gradually freezes out as the temperature of the liquid is slowly lowered toward T_g , and consequently the time correlation function $C(t)$ reflects the freezing of the α -process.

With very few exceptions, the normalized time correlation function $C(t)$ for one long system can be represented by the Kahlrausch-Williams-Watts (KWW) stretched exponential function

$$C(t) = \exp[-(t/\tau_0)^\beta] \quad (1)$$

where β ($0 < \beta \leq 1$) is the measure of the deviation from the single exponential function. If the nonexponential correlation function is due to the distribution of relaxation times, then a smaller β value indicates a wider relaxation time distribution. The mean relaxation time $\bar{\tau}$ is given by the area of $C(t)$ and is related to the intrinsic relaxation time τ_0 and β ,

$$\bar{\tau} = \int_0^\infty dt \exp[-(t/\tau_0)^\beta] = \frac{\tau_0}{\beta} \Gamma(\beta^{-1}) \quad (2)$$

In recent years, the laser-induced holographic grating relaxation (HGR) technique has also been introduced to investigate the tracer (or self) diffusion process of the photochromous dye molecule in various amorphous polymer hosts, above and below T_g .² The HGR tracer diffusion studies of the photochromous dye molecule in low molecular weight glass-forming liquids have also been carried out.³ Free volume theory has so far been used to interpret the HGR data. Recent efforts to correlate the tracer diffusion coefficient with the Stokes-Einstein (SE) equation have not been successful.³

In this communication, we provide both PCS and HGR data for ortho-terphenyl, a glass forming molecular liquid, and poly (propylene glycol). We show that the tracer diffusion coefficient of the photochromic dye molecule is closely related to the density fluctuation of the glass-forming host liquid. The dynamics of the glass transition can thus be probed by either using the PCS or the HGR technique. As shown here for the first time, the PCS technique provides more detailed information in that it now gives the density-density correlation function, whereas the HGR technique gives only the area of the correlation function.

Experimental

Orthoterphenyl (OTP) was purchased from Matheson, Coleman and Bell Manufacture Co. The sample was purified by repeated recrystallization. Poly(propane glycol) (PPG) polymer with molecular weight 4000 was purchased from Merck. Camphorquinone (CQ) and methyl red (MR) photochromic dyes were purchased from Aldrich and purified by recrystallization. The PCS experiments were carried out using similar optical setups as described previously.⁴

For the HGR experiment less than 0.5 wt % of CQ or MR was dissolved directly in the glass forming liquid. The sample was filtered into a thin glass-cell. The sample cell was first put in a cryostat (Oxford Instrument Inc.) through a special holder. The temperature readings of the cryostat was calibrated to within 0.2°K. The experimental setup for the HGR experiment was similar to that used in our previous studies,² with the exception of using a third He-Ne laser beam as the probing beam and employing a computer controlled electronic shutter and a chopper. With this modification, the set-up can be used to measure a wide dynamic range covering 10 orders of magnitude of diffusion coefficient from 10^{-5} to $10^{-15} \text{ cm}^2/\text{s}$.

Results and Discussion

Upon interacting with the Ar^+ laser radiation at 514.5 nm, MR undergoes a trans to cis isomerization. Thus, the relaxation time is associated with the HGR curve is related to the lifetime of the cis isomer τ_L and the relaxation time due to diffusion τ_D according to

$$\tau^{-1} = \tau_D^{-1} + \tau_L^{-1} \quad (3)$$

where τ_D is related to the tracer diffusion coefficient D according to $D = \frac{\lambda^2}{16\pi\tau\sin^2\theta/2}$.

Here θ is the crossing angle of the coherent writing laser beams and λ is the wavelength of the writing beams. By carrying out the HGR experiment at different crossing angle θ , we have separated τ_L and τ_D from the measured τ values. The experiment was repeated at different temperatures. The tracer diffusion coefficient and lifetime of MR in OTP plotted with respect to the reciprocal of the temperature are shown in Figs. 1 and 2, respectively. One notes that by lowering the temperature about 100 K from 357 to 255 K, the tracer diffusion coefficient of methyl red decreases more than 10 order of magnitude from 5.2×10^{-6} to $9.2 \times 10^{-16} \text{ cm}^2/\text{s}$. The variation of the lifetime τ_L is not as spectacular; it increases from 2.2 s at room temperature (298 K) to about 60s at 255 K.

While the lifetime variation with temperature for MR in OTP is Arrhenius, with activation energy approximately equal to 12.87 ± 0.3 kcal/mol, the temperature variation of D is not Arrhenius. Over the temperature range study, the diffusion data can be fit to the Williams-Landel-Ferry (WLF) equation

$$\log D(T) = \log D(T_g) + \frac{C_1^D(T - T_g)}{C_2^D + T - T_g} \quad (4)$$

where $D(T)$ is the tracer diffusion coefficient at temperature T (in K). The value of D at T_g is the extrapolated value, which is equal to $7 \times 10^{-18} \text{ cm}^2/\text{s}$. The WLF coefficient C_1^D and C_2^D are equal to 24.2 and 54.3 K, respectively.

The tracer diffusion data for CQ in PPG are given in Table 1 for the temperature varying from 286.0 to 233.2 K. The temperature dependence of D is not Arrhenius. The WLF equation fit to the diffusion data give $C_1^D = 13.5$ and $C_2^D = 35$ K. However, the value of C_1^D strongly correlates with the extrapolated value of the tracer diffusion

coefficient at T_g , which can not be measured.

The WLF equation is derived from free volume theory by assuming that D (neglecting the linear temperature factor) is given by⁵

$$D = D_\infty \exp(-B_D/f) \quad (5)$$

where f is the fractional free volume and B_D is a temperature independent parameter. D_∞ is the diffusion coefficient at high temperature when fractional free volume is large. Similarly, the shear viscosity η is expressed in terms free volume theory by⁶

$$\eta = \eta_\infty \exp(B/f) \quad (6)$$

where η_∞ is the viscosity at high temperature. The temperature independent constant β is in general larger than B_0 . The difference is argued as due to the fact that rearrangement of the liquid structure is needed to provide enough free volume for the diffusant to jump into the available space.⁶

It follows from Eqs. (5) and (6) that

$$D\eta^\gamma = \text{constant} \quad (7)$$

where $\gamma = B_D/B$ is in general less than 1. If $\gamma = 1$, then D follows the temperature dependence of η . For systems with D following the Stokes Einstein (SE) equation, one has $\gamma = 1$. For systems in which the viscoelastic effect prevails γ will in general be less than 1.

Using the viscosity data provided in ref. 1, we have found that $\gamma = 0.75$ for the tracer diffusion data for CQ in PPG. For MR in OTP, we find by using the viscosity data of Laughlin et al.⁸ that $\gamma = 0.80$ for temperature below 260 K. Above 300 K, we obtain $\gamma = 1$. The crossover from $\gamma = 0.80$ to $\gamma = 1$ occurs in the vicinity of 273 K. The $\gamma = 0.80$ value for MR in OTP compares quite well with the result of $\gamma = 0.79$ for the Aberchrome 540 (ACR) dye in OTP investigated by Lohfink et al.³

The tracer diffusion coefficient D is related to the friction coefficient ζ due to the solvent molecules by

$$D = \frac{kT}{\zeta} \quad \text{and the surrounding} \quad (8)$$

If the intermolecular interaction potential between the tracer

solvent molecules is given by $\sum_j u(|\underline{r} - \underline{r}_j|)$, where \underline{r} and \underline{r}_j are the position of the tracer and solvent molecule j , respectively,

By taking the Fourier transform of the intermolecular potential and neglecting the interaction between tracer molecules (valid in very dilute tracer concentration), one can show that the tracer diffusion coefficient D is related to the time correlation function of the density fluctuation $C(t)$ by⁹

$$D = kT / \left[|F_q|^2 \int_0^\infty dt C(t) \right] \quad (9)$$

when F_q is the intermolecular force averaged over the distance of q^{-1} , q is the amplitude of the scattering vector. For dense fluids, F_q is expected to be independent of q as the averaged inter-molecular force should be uniform. The time integral over the correlation function $C(t)$ is the mean relaxation time $\bar{\tau}$, given in Eq. (2). Thus, Eq. (9) indicates that D is proportional to $T/\bar{\tau}$. This prediction is clearly born out in the CQ in PPG as shown in Table I. Other glass forming liquids also yield similar results. The mean relaxation times $\bar{\tau}$ for OTP and PPG were obtained from PCS experiments.

Acknowledgements: This research is supported by the Office of Naval Research.

References

1. C. H. Wang, G. Fytas, D. Lilge and Th. Dorfmueller, *Macromolecules*, 1981, **14**, 363.
2. Zhang, J., Wang, C. H., *Macromolecules*, 1987, **20**, 683 and references cited herein.
3. Lohfink, M. et al., Translational Diffusion in Supercooled Liquids at the Glass Transition (preprint).
4. Xia, J. L., Wang, C. H. *J. Chem. Phys.* 1990, **94**, 3229.
5. Fujita, H., Fortsch, Hochpolym. 1961, **3**, 1.
6. Ferry, J. D., Viscoelastic Properties of Polymers, 3rd Ed. (Wiley, New York 1980).
7. Vrentas, J. S., Duda, J.L., *J. Appl. Polym. Sci.* 1977, **21**, 1715, and references cited herein.
8. Laughlin, W. T., Uhlmann, D R., *J. Phys. Chem.* 1972, **67**, 2317. Cukiermann, M., Lane, J. W., Uhlmann, W. T., *J. Chem. Phys.* 1973, **59**, 3639.
9. C. H. Wang and S. S. Gong (to be published).

Table I

$\bar{\tau}$ tracer diffusion data of CQ in PPG (MW = 4000) at various temperatures.

T(K)	$\bar{\tau}$ (s)	D (cm^2/s)	$\bar{\tau}D$ (cm^2)
286.0	---	2.3×10^{-9}	---
273.5	---	9.1×10^{-10}	---
259.6	---	2.9×10^{-10}	---
248.7	---	8.9×10^{-11}	---
240.3	---	2.4×10^{-11}	---
233.2	---	7.0×10^{-12}	---
225.1	9.5×10^{-5}	5.3×10^{-12}	5.0×10^{-16}
220.0	1.0×10^{-3}	6.0×10^{-13}	6.0×10^{-16}
215.4	6.0×10^{-3}	1.1×10^{-13}	6.6×10^{-16}
210.2	1.5×10^{-1}	4.0×10^{-15}	6.0×10^{-16}

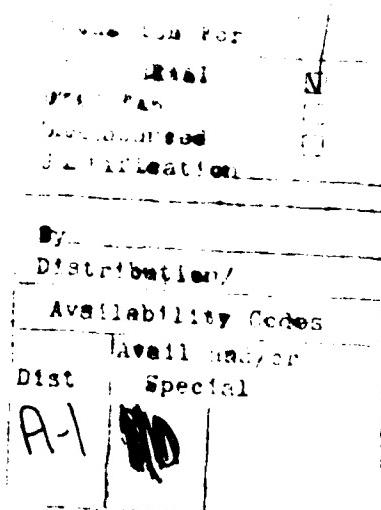


Figure 1: Temperature dependence of the tracer diffusion coefficient of MR in OTR.

Figure 2: Temperature dependence of the lifetime of MR in OTR.